THE KINETICS AND MECHANISM OF VINYL POLYMERIZATION

BY

ROBERT WARREN KELL

B.Ed., Southern Illinois State Teachers College, 1937

M.S., University of Illinois, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1941

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THE KINETICS AND MECHANISM OF VINYL POLYMERIZATION

INTRODUCTION

Due to lack of a satisfactory analytical procedure for following the kinetics of polymerization reactions in dilute solutions, a major portion of the previous studies in this field has been carried out without a diluent,[1] or over a wide range in mole fraction of solvent. Under such conditions, the relative effects of the change in reaction medium on the various steps of the polymerization process make accurate deductions as to the mechanism of the reaction complex and difficult. This investigation was undertaken to determine the kinetics in dilute solution, making use of the polarimetric technique for following the polymerization recently reported by Marvel, Cooke and Dec.[2]

EXPERIMENTAL AND DISCUSSION OF RESULTS

The *d-sec*-butyl α-chloroacrylate used in these experiments was prepared by the method of Marvel, Cooke and Dec.[2] It was stored over hydroquinone and samples were twice redistilled immediately before use since the uninhibited monomer polymerized appreciably in a few days at room temperature. The benzoyl peroxide used was proven to be essentially pure by analysis. Standard solutions of the monomer and the peroxide in pure dry dioxane[3] were prepared in volumetric flasks and were mixed in various ratios in sufficient volume to fill 1-dm. jacketed polarimeter tubes. Water from a thermostat regulated to $\pm 0.2°$ was circulated through the jacket around the tubes and the rotations of the reaction mixture were observed at specified intervals.

On the basis of the assumption that the specific rotation of the monomeric units in the polymer chains is independent of the degree of polymerization, the concentration of monomer is obtained as follows:

$$[M]_t = [M]_o \frac{a_t - a_\infty}{a_o - a_\infty}$$

In this expression, $[M]_o$ is the initial monomer concentration, $[M]_t$ that at time t, a_o is the observed initial rotation, a_t that at time t,

and a_∞ the final rotation when the polymerization is complete.

The measurements of the benzoyl peroxide catalyzed polymerization of *d-sec*-butyl *a*-chloroacrylate in dilute dioxane solution have clearly demonstrated the rate of the reaction to be proportional to the monomer concentration ([M]) and to the square root of the catalyst concentration ([Cat]) over a wide range in the ratio of the initial concentrations and for practically the entire course of the polymerization.

$$-\frac{d\,[M]}{dt} = k\,[Cat]^{1/2}\,[M]$$

From the values for the rate constants at five different temperatures, the overall activation energy for the reaction was found to be 15,200 $\pm$ 400 cals.

In terms of a mechanism for the polymerization, the only plausible explanation for the observed kinetics is a sequence of reactions involving (A), a first-order chain-initiating decomposition of the catalyst, (B), a chain-propogating reaction of monomer with an active (free radical) chain generated by (A), and (C), a second-order chain-stopping reaction of two active free radicals.

The most logical course for the chain initiating process (A) is the decomposition of benzoyl peroxide to generate free radicals.[4]

$$(C_6H_5CO_2)_2 \rightarrow 2C_6H_5CO_2\cdot$$

$$C_6H_5CO_2\cdot \rightarrow CO_2 + C_6H_5\cdot$$

It has frequently been suggested that step (B), the reaction involving the growth of polymeric chains, proceeds through a free-radical mechanism,[5] particularly for certain cases initiated photochemically.[6] It is in this step that monomer is transformed into polymer and it is, therefore, the rate of this step which governs the rate of polymerization.

The destruction of the free radical activity leading to polymerization can be accomplished only through a bimolecular reaction involving two of the radicals. This reaction may involve coupling of the two radicals or, more probably, a disproportionation to form one saturated and one unsaturated molecule.

SUMMARY

An investigation of the kinetics of the benzoyl peroxide-catalyzed polymerization of *d-sec*-butyl α-chloroacrylate in dilute dioxane solution at several temperatures between 26° and 68° has shown the rate of the reaction to be accurately proportional to the monomer concentration and to the square root of the catalyst concentration.

These results are strong support for a mechanism of the polymerization involving (A), a first-order chain-initiating decomposition of the catalyst into free radicals, (B), a second-order chain-propagating reaction involving reaction of an active (free radical) chain with a monomer molecule, and (C), a second-order chain-stopping reaction involving two active free radicals.

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VITA

The writer was born in St. Louis, Missouri, on July 6, 1915. He attended the public schools of that city and was graduated from the Beaumont High School of St. Louis in 1933. In September, 1933, he entered the Southern Illinois State Teachers College and was granted the degree of Bachelor of Education in June, 1937. He entered the Graduate School of the University of Illinois the following September and was granted the degree of Master of Science in June, 1938. During the years 1938-1941, he served as an assistant for Organic Chemical Manufacturers.